Polyhedron 33 (2012) 327–335

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and metal coordination chemistry of (phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid, [2-C_5H_4N]$CH_2P(S)(SH)(Ph)$

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ARTICLE INFO

Article history:
Received 29 September 2011
Accepted 22 November 2011
Available online 29 November 2011

Keywords:
Pyridyl
Dithiophosphinic acid
Cd(II)
Pt(II) complexes
Protonation constants
Complexation constants
X-ray crystal structures

ABSTRACT

A three-step synthesis for the bifunctional ligand (phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid, [2-C_5H_4N]$CH_2P(S)(SH)(Ph)$ (**3-H**), was developed. The molecule was characterized by spectroscopic methods, and single crystal X-ray diffraction analysis, and the molecule found to exist in a zwitterionic form (**3′**). Protonation constants for **3′** were measured spectrophotometrically in 0.1 M $NaClO_4$ aqueous solution. The coordination chemistry of **3′** toward $CdCl_2$ and $PtCl_2$ was explored, and the complexes $[Cd(\mathbf{3'})Cl_2]_2$ and $[Pt(\mathbf{3}^-)_2]\cdot CHCl_3$ were isolated and structurally characterized by single crystal X-ray diffraction methods. Complexation constants for **3′** with Cd(II), Zn(II) and La(III), as a function of pH, were measured by titration techniques. An initial effort to prepare the [pyridin-bis(2,6-yl-methylphosphinodithioic acid)] analog of **3-H** led to the formation and isolation of (phenyl)(6-methylpyridin-2-ylmethyl)phosphinodithioic acid, [2-C_5H_3N(6-CH_3)]$CH_2P(S)(SH)(Ph)$ (**6-H**), that was characterized by spectroscopic methods and single crystal X-ray diffraction analysis. As found with **3-H**, **6-H**, adopts a zwitterionic structural form (**6′**).

1. Introduction

The syntheses and chemistry of mono-dithiophosphoric, $(RO)_2P(S)(SH)$, -dithiophosphonic, (RO)(R)P(S)(SH), and -dithiophosphinic, $R_2P(S)(SH)$, acids have been widely studied, and numerous applications for the reagents have been developed [1–3]. The coordination chemistry of the respective anions has also attracted much attention as these species display a remarkable diversity in coordination modes with *s*-, *p*-, *d*- and *f*-block metal cations, and much of that activity has been reviewed [1–6]. Few bis-dithiophosphorus acids or their conjugate bases have been reported, but Kuchen and coworkers [7] have outlined a preparation for the bis(dithiophosphinic acids), $[R_2P(S)(SH)]_2(CH_2)_n$ (n = 4–10). Davies and coworkers [8] have also described a synthesis and coordination chemistry for a bis(dithiophosphinate), $Li_2[PhP(S)_2(CH_2)]_2$. In nearly all examples, the organyl groups, R, in the acids and their anionic conjugate bases are simple alkyl or aryl fragments that do not contain additional donor site functionality. In our own case, we are interested in attachment of dithiophosphorus acid fragments to organic platforms that also carry additional harder or softer donor sites such that unique asymmetric coordination fields may be produced. We report here the synthesis and selected coordination chemistry of one such target ligand type, [2-C_5H_4N]$CH_2P(S)(SH)$-(Ph) (**3-H**), that contains a pyridin-2-ylmethyl fragment and a dithiophosphinic acid group.

2. Experimental

2.1. Materials and general procedures

Organic reagents were purchased from Aldrich Chemical Co. and used as received. Organic solvents were rigorously dried according to standard procedures. The $CdCl_2$ and $PtCl_2$ for metal complex preparations were purchased from Ventron. The metal perchlorates for the titration analyses were purchased from VWR and Strem Chemicals. Titrations were performed with solutions prepared by using deionized water (Milli-Q, Waters Corp) of >18 M Ω cm^{-1} resistivity. Infrared spectra were recorded with a Tensor 200 FTIR spectrometer, and NMR spectra were recorded with Bruker FX-250, Avance 300 and Avance 500 NMR spectrometers. External chemical shift standards, Me_4Si (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P), were employed. Mass spectra were measured in the positive ion mode unless noted otherwise at the UNM Mass Spectrometry Facility, and elemental analyses were performed by Galbraith Laboratories.

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doi:10.1016/j.poly.2011.11.041

2.2. Experimental procedures

2.2.1. Ligand syntheses

*2.2.1.1. (Phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid (**3-H**).* A sample of $PhP(OEt)_2$ (0.78 g, 3.9 mmol) was added to a solution of 2-bromomethylpyridine (0.68 g, 3.9 mmol) in dry CH_3CN (15 mL), and the mixture was heated under reflux (4 h). The CH_3CN was vacuum evaporated, the residue dissolved in CH_2Cl_2 (20 mL), and the resulting solution washed with water (2 × 10 mL). The organic phase was separated, vacuum evaporated, and the residue purified by column chromatography (SiO_2, 70–230 mesh, elution with CH_2Cl_2/MeOH, 80/20). (Phenyl)(pyridine-2-ylmethyl)phosphinic acid ethyl ester, 2-[(Ph)(EtO)P(O)CH_2]C_5H_4N (**1**), was obtained as a colorless liquid. Yield: 0.90 g, 87%. IR (KBr, cm^{-1}): ν = 1226 (s, ν_{PO}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 39.6. ^1H NMR ($CDCl_3$): δ = 1.27 (t, J_{HH} = 7.0 Hz, 3H, OCH_2CH_3), 3.57 (d, J_{PH} = 18.0 Hz, 2H, PCH_2), 3.88–3.98 (m, 1H, $OCH_AH_BCH_3$), 4.05–4.15 (m, 1H, $OCH_ACH_BCH_3$), 7.10 (t, J_{HH} = 6.0 Hz, 1H, *Ar-H*), 7.27–7.71 (m, 7H, *Ar-H*), 8.2 (d, J_{HH} = 4.7 Hz, 1H, *Ar-H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 16.3 (OCH_2CH_3), 40.8 (d, J_{PC} = 92.3 Hz, PCH_2), 61.0 (d, J_{PC} = 6.2 Hz, OCH_2CH_3), 121.6 (d, J_{PC} = 2.5 Hz, *Ar*), 124.4 (d, J_{PC} = 3.9 Hz, *Ar*), 128.3 (d, J_{PC} = 12.5 Hz, *Ar*), 130.2 (d, J_{PC} = 127.6 Hz, *Ar*), 131.6 (d, J_{PC} = 9.8 Hz, *Ar*), 132.2 (d, J_{PC} = 1.9 Hz, *Ar*), 136.2(*Ar*), 149.2(*Ar*), 152.4 (d, J_{PC} = 7.2 Hz, *Ar*). Mass spectrum (ESI): *m/z* = 262.09 [M+H$^+$], 284.07 [M+Na$^+$]. *Anal.* Calc. for $C_{14}H_{16}NO_2P$: C, 64.36; H, 6.17; N, 5.36. Found: C, 61.18; H, 6.04; N, 5.19%.

A 100 mL three-necked flask, outfitted with an addition funnel, was charged with a sample of **1** (0.561 g, 2.15 mmol), frozen with liquid nitrogen, evacuated and backfilled with nitrogen. Dry toluene (10 mL) was added followed by dropwise addition (10 min, 23 °C) of DIBAL-H solution (Aldrich, 1 M in toluene, 8.6 mL). During the addition, the solution became light yellow in color. The mixture was then heated (50 °C) and stirred (12 h). The resulting mixture was cooled (−78 °C) and cautiously quenched with 4 M NaOH solution (4 mL). The phases were allowed to separate, and the organic phase was removed under nitrogen by syringe to another Schlenk vessel containing sulfur (0.137 g, 4.39 mmol). The remaining aqueous phase was extracted with fresh toluene (2 × 5 mL), and the organic layers were added to the vessel containing the first organic fraction and sulfur. The mixture was stirred (23 °C, 1 h) and then gently heated (70 °C, 4 h). A solid formed that was recovered by filtration and washed with toluene leaving a white solid (phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid, (**3-H**), that was crystallized by slow evaporation from MeOH/CH_3CN (1/1)solution. Yield: 0.38 g (67%). Mp 238–240 °C. The compound is soluble in DMSO and DMF, slightly soluble in MeOH, EtOH, $CHCl_3$, CH_3CN and THF, and it has slight solubility in water. IR (KBr, cm^{-1}): ν = 652 (vs, ν_{PS}), 543 (s, ν_{PS}). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 64.0. ^1H NMR (DMSO-d_6): δ = 3.69 (d, J_{PH} = 12.5 Hz, 2H, PCH_2), 7.36 (br, 3H, *Ph*), 7.48 (d, J_{HH} = 8.0 Hz, 1H, *Pyr-H*$_3$), 7.79 (dd, J_{HH} = 6.0 Hz, 1H, *Pyr-H*$_4$), 7.99–8.03 (m, 2H, *Ph*), 8.31 (dd, J_{HH} = 7 Hz, 1H, *Pyr-H*$_5$), 8.72 (d, J_{HH} = 5 Hz, 1H, *Pyr-H*$_6$). $^1H\{^{31}P\}$ NMR (DMSO-d_6): δ = 3.69 (s, 2H, PCH_2), 7.36 (br, 3H, *Ph*), 7.48 (d, J_{HH} = 7 Hz, 1H, *Pyr-H*$_3$), 7.79 (dd, J_{HH} = 6 Hz, 1H, *Pyr-H*$_4$), 8.02 (d, J_{HH} 3 Hz, 2H, *Ph*), 8.31 (dd, J_{HH} = 7 Hz, 1H, *Pyr-H*$_5$), 8.72, (br, 1H, *Pyr-H*$_6$), 15.34 (br, s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ = 52.1 (d, J_{PC} = 36.4 Hz, PCH_2), 124.0. 127.1 (d, J_{PC} = 11.9 Hz), 127.7, 129.4, 130.5 (d, J_{PC} = 10.7 Hz), 140.0, 142.5 (d, J_{PC} = 76 Hz), 143.9, 150.8 (d, J_{PC} = 6.8 Hz). Mass spectrum (HRESI): *m/z* = [M+H$^+$] 266.0223; $C_{12}H_{13}NP^{32}S_2$ requires 266.0227, [M+Na$^+$] 288.0045; $C_{12}H_{12}NNaP^{32}S_2$ requires 288.0047. *Anal.* Calc. For $C_{12}H_{12}NPS_2$: C, 54.32; H, 4.56; N, 5.28; S, 24.17. Found: C, 54.80, H, 4.65; N, 5.33; S, 23.95%.

*2.2.1.2. (Phenyl)(6-methyl-pyridin-2-ylmethyl)phosphinodithioic acid (**6-H**).* A sample of **4** (0.941 g, 2.21 mmol) [9] in dry THF (15 mL) was treated dropwise under nitrogen with DIBAL-H solution (Aldrich, 1 M in THF, 25.4 mL) over 10 min (23 °C). The mixture was stirred (23 °C, 24 h) and diethyl ether (15 mL) was added. This mixture was cooled (0 °C) and quenched cautiously with 6 M NaOH (40 mL). Following vigorous gas evolution, the layers were separated, and the organic layer was transferred via syringe to another flask, dried over Na_2SO_4 and then transferred to a flask containing sulfur (0.27 g, 8.4 mmol). The mixture was refluxed (12 h), filtered and the filtrate evaporated. The remaining residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH, 90/10). (Phenyl)(6-methylpyridin-2-ylmethyl)phosphinodithioic acid (**6-H**) was recovered as a colorless solid that was crystallized from MeOH/$CHCl_3$, 5/1. Yield: 0.12 g (20%). Mp 212–214 °C. IR (KBr, cm^{-1}): ν = 646 (vs, ν_{PS}), 549 (s, ν_{PS}). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 63.8. ^1H NMR (DMSO-d_6): δ = 2.65 (s, 3H, CH_3), 3.71 (d, J_{PH} = 13.0 Hz, 2H, PCH_2), 7.22 (d, J_{HH} = 8.0 Hz, 1H, *Ar*), 7.39 (br, 3H, *Ar*), 7.66 (d, J_{HH} = 7.5 Hz, 1H, *Ar*), 7.99–8.07 (m, 2H, *Ar*), 8.20 (t, J_{HH} = 7.5 Hz, 1H, *Ar*), 14.89 (br, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ = 19.1 (CH_3), 51.7 (d, J_{PC} = 35.7 Hz, PCH_2), 124.2, 124.6, 127.1 (d, J_{PC} = 11.6 Hz), 129.4, 130.6 (d, J_{PC} = 10.4 Hz), 142.8 (d, J_{PC} = 76.0 Hz), 143.8, 150.4, 151.4. Mass spectrum (ESI): *m/z* = [M+H$^+$] 280.03, [M+Na$^+$] 302.02. *Anal.* Calc. for $C_{13}H_{14}NPS_2$: C, 55.89; H, 5.05; N, 5.01; S, 22.95. Found: C, 55.46; H, 5.05; N, 4.92; S, 23.13%.

2.2.2. Coordination complex syntheses

2.2.2.1. Cadmium(II) complex. Compound **3′** (0.052 g, 0.19 mmol) and $CdCl_2$ (0.018 g, 0.1 mmol) were combined in a mixture of $CHCl_3$ (3 mL) and MeOH (3 mL), and the solution refluxed (12 h). A solid, $[Cd(\mathbf{3'})Cl_2]_2$, formed during heating. After cooling (23 °C), the solid was collected by filtration. Yield: 0.04 g (90%). IR (KBr, cm^{-1}): ν = 629 (vs, ν_{PS}), 534 (s, ν_{PS}). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 66.9. ^1H NMR (DMSO-d_6): δ = 3.79 (d, J_{PH} = 13.0 Hz, 2H, P*CH*2), 4.45 (br, 1H, N*H*), 7.42 (br, 3H, *Ph*), 7.49 (br, 1H, *Pyr*), 7.79 (br, 1H, *Pyr*), 8.04–8.08 (m, 2H, *Ph*), 8.29 (br, 1H, *Pyr*), 8.75 (d, J_{HH} = 5 Hz, 1H, *Pyr*). Mass spectrum (HRMS-negative ion mode): *m/z* = [M−H$^-$] 447.8478; $C_{12}H_{11}{}^{114}Cd^{35}ClNP^{32}S$ requires 447.8481. *Anal.* Calc. for $C_{12}H_{12}CdCl_2NPS_2$: C, 32.13; H, 2.70; N, 3.12. Found: C, 34.18; H, 3.10, N, 2.91%.

2.2.2.2. Platinum(II) complex. Compound **3′** (0.099 g, 0.37 mmol) and $PtCl_2$ (0.050 g, 0.19 mmol) were initially combined in CH_3CN (10 mL), and the solution refluxed (12 h). The resulting yellow solution was evaporated, the residue was dissolved in $CHCl_3$/MeOH (1:5), and the resulting solution refluxed (12 h). A clear reddish brown solution was obtained that was allowed to slowly evaporate leaving yellow crystals, $[Pt(\mathbf{3}^-)_2]$. IR spectra (KBr, cm^{-1}): ν = 653 (vs, ν_{PS}), 523 (s, ν_{PS}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 55.5. Mass spectrum (HRMS): *m/z* = [M+H$^+$] 723.9883; $C_{24}H_{23}N_2P_2{}^{32}S_4{}^{195}Pt$ requires 723.9867.

2.2.3. Ligand pK_a and metal stability constant determinations

The spectrophotometric titration experiments were carried out with a 1.0 cm quartz flow cell (VWR) placed in a Varian 300 Cary 1E UV–Vis spectrophotometer controlled by Cary Win UV Scan Application version 02.00(5) software. This was connected to an external, temperature controlled titration cell maintained at 25.0 ± 0.1 °C. The solution was continually circulated from the external cell to the flow cell in the spectrophotometer using a peristaltic pump. A VWR sympHony™ SR60IC pH meter with a VWR sympHony™ gel epoxy semi-micro combination pH electrode was used for all pH readings, which were recorded in the external cell. Equilibration and mixing were allowed for by circulating the solution for 15 min before each new spectrum was recorded. Fitting of theoretical absorbance versus pH or log[*M*] curves was accomplished using the SOLVER module of EXCEL [10]. For a set